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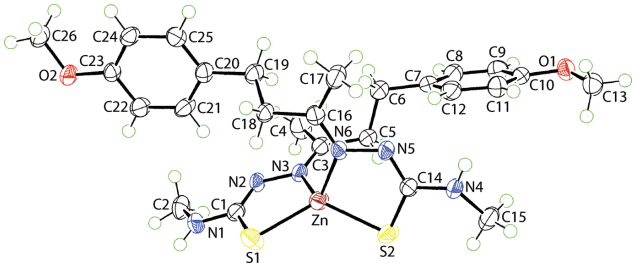
Crystal structure of bis{*N*-methyl-*N*′-[3-(4-methoxyphenyl)-1-methylpropane-1-ylidene]carbamohydrazonothioato}zinc(II), $C_{26}H_{36}N_6O_2S_2Zn$



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Abstract

$C_{26}H_{36}N_6O_2S_2Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1777(5)$ Å, $b = 12.3828(7)$ Å, $c = 13.3137(7)$ Å, $\alpha = 102.157(5)°$, $\beta = 101.395(4)°$, $\gamma = 100.771(4)°$, $V = 1408.14(14)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0489$, $wR_{ref}(F^2) = 0.1147$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

4-Methyl-3-thiosemicarbazide (Alfa Aesar), 4-(4-methoxyphenyl)-2-butanone (Sigma Aldrich), zinc acetate dihydrate (Fluka), absolute ethanol (Merck) and acetonitrile

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Table 1: Data collection and handling.

Crystal:	Colourless slab
Size:	0.16 × 0.12 × 0.04 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.06 mm^{-1}
Diffractometer, scan mode:	Oxford Diffraction SuperNova, ω
θ_{max}, completeness:	28.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12413, 6335, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4742
$N(param)_{refined}$:	346
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn	0.91082(4)	0.22680(3)	0.25162(3)	0.02339(11)
S1	1.05901(9)	0.21312(8)	0.40419(6)	0.0312(2)
S2	0.95685(9)	0.17416(7)	0.08882(6)	0.02683(19)
O1	0.2828(2)	0.17380(17)	−0.33342(15)	0.0252(5)
O2	0.7703(2)	0.47250(17)	0.85343(15)	0.0241(5)
N1	0.9344(3)	0.1265(2)	0.54031(19)	0.0246(6)
H1N	1.0282(17)	0.134(3)	0.576(2)	0.030*
N2	0.7560(3)	0.12345(19)	0.39549(18)	0.0200(5)
N3	0.7260(3)	0.14303(19)	0.29480(18)	0.0198(5)
N4	0.8974(3)	0.2964(2)	−0.05031(19)	0.0239(6)
H4N	0.871(3)	0.3557(17)	−0.068(2)	0.029*
N5	0.8602(3)	0.37436(19)	0.10833(17)	0.0189(5)
N6	0.8690(3)	0.3710(2)	0.21359(17)	0.0184(5)
C1	0.9009(3)	0.1484(2)	0.4448(2)	0.0226(6)
C2	0.8186(4)	0.0648(3)	0.5811(2)	0.0284(7)
H2A	0.749031	0.112787	0.599245	0.043*
H2B	0.867998	0.044831	0.644554	0.043*
H2C	0.760462	−0.004687	0.526930	0.043*
C3	0.5837(3)	0.1119(2)	0.2430(2)	0.0222(6)
C4	0.4595(4)	0.0630(3)	0.2906(3)	0.0347(8)
H4A	0.472653	−0.010555	0.302092	0.052*
H4B	0.359474	0.052462	0.242217	0.052*
H4C	0.465267	0.115213	0.358513	0.052*
C5	0.5419(3)	0.1171(2)	0.1300(2)	0.0223(6)
H5A	0.484133	0.040520	0.085944	0.027*
H5B	0.637342	0.136505	0.106805	0.027*
C6	0.4458(3)	0.2031(3)	0.1083(2)	0.0253(7)
H6A	0.351607	0.186403	0.133502	0.030*
H6B	0.505016	0.280821	0.148396	0.030*
C7	0.4030(3)	0.1981(2)	−0.0083(2)	0.0225(6)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C8	0.2708(3)	0.1227(3)	−0.0763(2)	0.0257(7)
H8	0.204348	0.075593	−0.048087	0.031*
C9	0.2344(3)	0.1153(2)	−0.1840(2)	0.0245(7)
H9	0.143864	0.063324	−0.228777	0.029*
C10	0.3300(3)	0.1836(2)	−0.2266(2)	0.0207(6)
C11	0.4633(3)	0.2585(2)	−0.1605(2)	0.0235(6)
H11	0.530362	0.304856	−0.188890	0.028*
C12	0.4976(3)	0.2648(3)	−0.0531(2)	0.0250(7)
H12	0.588541	0.316373	−0.008467	0.030*
C13	0.3930(4)	0.2258(3)	−0.3822(2)	0.0291(7)
H13A	0.419644	0.308402	−0.352819	0.044*
H13B	0.349675	0.207772	−0.458899	0.044*
H13C	0.485239	0.196625	−0.368383	0.044*
C14	0.8999(3)	0.2903(2)	0.0509(2)	0.0201(6)
C15	0.9007(4)	0.2041(3)	−0.1360(2)	0.0348(8)
H15A	0.938601	0.145388	−0.106882	0.052*
H15B	0.968623	0.232906	−0.177710	0.052*
H15C	0.797169	0.171425	−0.181665	0.052*
C16	0.8408(3)	0.4583(2)	0.2724(2)	0.0201(6)
C17	0.8037(4)	0.5563(3)	0.2320(2)	0.0280(7)
H17A	0.875540	0.578981	0.190441	0.042*
H17B	0.812110	0.620418	0.292006	0.042*
H17C	0.699046	0.533705	0.187045	0.042*
C18	0.8486(3)	0.4620(3)	0.3864(2)	0.0213(6)
H18A	0.917021	0.535177	0.430815	0.026*
H18B	0.894879	0.400237	0.404305	0.026*
C19	0.6920(3)	0.4494(3)	0.4144(2)	0.0236(6)
H19A	0.643699	0.509777	0.395146	0.028*
H19B	0.624222	0.374943	0.372579	0.028*
C20	0.7088(3)	0.4578(2)	0.5309(2)	0.0212(6)
C21	0.7537(3)	0.3734(3)	0.5749(2)	0.0258(7)
H21	0.770734	0.308709	0.530142	0.031*
C22	0.7742(3)	0.3810(3)	0.6817(2)	0.0255(7)
H22	0.805331	0.321999	0.709504	0.031*
C23	0.7495(3)	0.4744(2)	0.7491(2)	0.0193(6)
C24	0.7044(3)	0.5595(3)	0.7070(2)	0.0227(6)
H24	0.686532	0.623728	0.751709	0.027*
C25	0.6853(3)	0.5506(2)	0.5986(2)	0.0223(6)
H25	0.655293	0.609832	0.570664	0.027*
C26	0.7232(4)	0.5576(3)	0.9225(2)	0.0270(7)
H26A	0.783559	0.633148	0.926034	0.040*
H26B	0.739633	0.544784	0.993571	0.040*
H26C	0.614448	0.553090	0.894898	0.040*

(Merck) were of analytical grade and used as purchased. The Schiff base ligand, LH, was prepared as described in the literature [5]. Zinc acetate dihydrate (0.220 g, 10 mmol) was dissolved in hot ethanol (20 mL) and added to a solution of LH (0.530 g, 20 mmol) in hot absolute ethanol (20 mL) while stirring for 30 min. The white precipitate was filtered, washed with cold ethanol and dried in vacuo. Single crystals were grown at room temperature from the slow evaporation of an acetonitrile/absolute ethanol (2:1 *v*/*v*) solution. Yield: 89%. **M. Pt**: 434–435 K. **FT-IR** (ATR (solid) cm^{-1}): 3366 ν(N—H), 1606 ν(C=N), 1239 ν(N—N), 516 ν(Zn—N), 439 ν(Zn—S). **UV-Visible**: λ_{max} (nm; ϵ (L mol^{-1} cm^{-1})): 239 (76,913), 279 (51,641). **ICP-AES**: Experimental %Zn = 11.05, Theoretical %Zn = 11.00.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. The N-bound H atoms were refined with N—H = 0.88 ± 0.01 Å, and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Comment

Metal complexes derived from thiosemicarbazones, $R^1R^2C{=}N{-}N(R^3){-}C(=S)NR^4R^5$, for $R^{1\text{–}5}$ = H/alkyl/aryl have huge potential variability in composition and many are well-documented as having therapeutic applications and for their use as imaging agents [6]. Among the former, zinc(II) complexes are prominent with reports of their potential as anti-bacterial [7], anti-cancer [8] and anti-viral [9] agents. In continuation of biological studies of different metal complexes of thiosemicarbazones [10] and of supporting structural studies of zinc thiosemicarbazones [11, 12], herein the synthesis, characterisation as well as the crystal and molecular structures of $Zn[(4\text{-}MeOC_6H_4)CH_2CH_2C(Me){=}NN{=}C(S)N(H)Me]_2$, (I), are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) which shows the zinc(II) centre to be bis-chelated in a N,S-fashion by two mono-anionic thiosemicarbazato ligands. For the S1-ligand, the Zn—S1 [2.2680(9) Å] and Zn—N3 [2.065(2) Å] bond lengths are shorter and longer, respectively, than the equivalent Zn—S2 [2.2739(8) Å] and Zn—N6 [2.038(2) Å] bonds for the S2-ligand. Compared with the structure of the uncoordinated ligand [5], the C—S [C1—S1 = 1.760(3) Å and C14—S2 = 1.755(3) Å] and [C1 = N2 = 1.308(4) Å and C14 = N5 = 1.310(3) Å] bond lengths in (I) have elongated and shortened, respectively, compared with the C1 = S1 [1.6943(13) & 1.6881(13) Å for the two independent molecules] and C1—N2 [1.3563(17) & 1.3616(17) Å] bond lengths of the acid, confirming the newly formed thiolate and imine bonds in (I) (see the figure).

The N_2S_2 at Zn donor set defines an approximate tetrahedral geometry with the range of angles being 87.10(7)° for the S1—Zn—N3 chelate angle to 127.45(7)° for S1—Zn—N6. The mode of coordination of the ligands leads to the formation of five-membered chelate rings. These are best described as having an envelope conformation with Zn lying 0.131(4) Å out of the least-squares plane defined by the remaining four atoms [r.m.s. deviation = 0.018 Å] for the S1-ligand. The envelope description is more pronounced for the S2-ligand with the equivalent parameters being 0.229(4) and 0.006 Å, respectively. The dihedral angle formed between the best planes through the rings is 79.95(5)°.

As discussed recently [11], are now more than ten known mononuclear complexes described by the general formula $Zn[SC(NHR^4)=NNCR^1R^2]_2$ where the R groups are non-coordinating and which crystallise solvent-free. To a first approximation, each of these structures resembles (I) but, with varying degrees of distortion from the ideal tetrahedral geometry evident, as manifested in the dihedral angle between the chelate rings. The chelate/chelate angles in the literature structures vary from 60.10(5) to 89.65(5)°. Interestingly, these angles are calculated for the two independent molecules in the asymmetric unit of the complex with $R^1 = R^4 = Ph$ and $R^2 = Me$ [13], suggesting an influence of molecular packing effects on the adopted conformation.

In the crystal of (I), thioamide-N—H···O(methoxy) hydrogen bonds [N1—H1n···$O1^i$: H1n···$O1^i$ = 2.32(2) Å, N1···$O1^i$ = 3.187(3) Å with angle at H1n = 174(3)° and N4—H4n···$O2^{ii}$: H4n···$O2^{ii}$ = 2.19(2) Å, N4···$O2^{ii}$ = 3.049(3) Å with angle at H4n = 166(2)° for symmetry operations (i) $1+x$, y, $1+z$ and (ii) x, y, $-1+z$] are formed and lead to supramolecular layers perpendicular to [0 1 0]. In accord with the distance criteria in PLATON [14], no further directional interactions are apparent. Globally, centrosymmetrically related layers assemble into double-layers and inter-digitate along the *b*-axis.

A further analysis of the molecular packing was performed utilising Crystal Explorer 17 [15] and calculating the Hirshfeld surface and two-dimensional fingerprint plots (full and delineated) following literature procedures [16]. Consistent with the above description of the molecular packing, H···H contacts contribute 59.8% of all contacts to the surface. The most striking feature of the fingerprint plots are the well-defined spikes owing to the N—H···O hydrogen bonding. However, all H···O/O···H contacts contribute only 6.5% to the overall Hirshfeld surface. More prominent are H···C/C···H [14.3%] and H···S/S···S [11.9%] contacts; H···N/N···H [2.7%] contacts make only a minor contribution.

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